13. Physico-chemical Properties of Surface Active Agents. (V)

Molecular Weight and Viscosity of Polyoxyethylene Glycol Mono-Cetyl Ethers

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The molecular weights of mono-cetyl ethers of 2~30 membered polyoxythylene glycols (PEGCE) were determined in benzene by the cryoscopic method.

In determing the molecular weight by the cryoscopic method, it is necessary to extrapolate all measurements at different concentrations to infinite dilution, since Raoult's law holds for polymer solutions only at infinite dilution.

In general the molecular weight, M_c, calculated from "reduced depression," $\Delta T/c$, gradually decreases with a decrease in concentration. However, in the case of PEGCE the molecular weight, M_c, increased with dilution in concentrations lower than 3~4 mol percentage. In other words, the curve of M_c against the concentration C had a minimum at a definite concentration for a given PEGCE.

Such an anomalous phenomenon is an example of deviation from Raoult's law. Others have also reported the same on some polymers even at sufficient dilution (Gallaugher, A.F. and Hilbert, H.J.C.S. **58** 813 (1936); Kemp, A.R. and Peters, H. Ind. Eng. Chem. **34** 1097, 1192 (1942)).

In the present case the molecular weight M obtained by extrapolating the values of M_c at higher concentrations to infinite dilution was in good agreement with the one expected from the amount of ethylene oxides used in preparing the samples.

On the other hand, it was found that the curve of "reduced viscosity" η_{sp}/c versus C had a similar minimum point at a definite concentration as with the cryoscopic data.

It may be considered that a close relationship exists between those anomalies at low concentration in both cryoscopic and viscosity measurements.

Accordingly anomalous high values of η_{sp}/c at low concentration were neglected in determining the intrinsic viscosity $[\eta]$ of PEGCE.

The observed values of molecular weight and intrinsic viscosity are as follows.

Samples.	M_{theor}	M_{obs}	$[\eta]_{in CCl_4 25°} \cdot 10^2$
PC- 45	(440)	340	3.1
PC- 50	(460)	350	—
PC- 80	(594)	580	3.7
PC-100	(682)	680	3.8
PC-118	(762)	770	4.4
PC-143	(872)	870	4.6
PC-211	(1171)	930	4.9
PC-271	(1431)	1300	5.6
PC-313	(1620)	1600	6.1

(M_{theor} denotes mol. wt. evaluated from the amount of ethylene oxide).